

Non-covalent Interactions in Coals

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ABSTRACT

The interactions between bituminous coals and organic molecules can be quantitatively described using only two terms: interactions dependent on polarizability and acid/base interactions, especially hydrogen bonding. Except for groups having an unpaired electron (the coal radical sites), the same two forces so dominate coal-coal interactions that it is not necessary to invoke any others. Except for radical sites, HOMO-LUMO gaps are so large that π - π and charge transfer interactions (aromatic "stacking" interactions) are improbable.

DISCUSSION

The aromatic groups in coals can interact with each other by London Dispersion Interactions which increase as their polarizability increases. Electrostatic interactions due to the existence of dipoles or quadrupoles are also important. Charge transfer interactions, in which electron density is transferred from a donor molecule to an acceptor are not important. It makes no difference if the electrons in question are non-bonding or π electrons, charge transfer is not important. The remainder of this article is a justification of the foregoing assertions. The terms π - π and "stacking" interactions occur frequently in the coal literature and are not often defined. They seem to be used to mean associative interactions between aromatic systems due to electron transfer. That is the meaning assumed in this article.

Using gas chromatography to avoid complications caused by diffusion into coals¹, the isosteric heats of adsorption of a variety of organic molecules on the surface of Illinois No. 6 coal were measured.² As expected, noble gases and saturated hydrocarbons gave adsorption heats that are a linear function of molecular polarizability confirming that their interactions with the coal surface are dominated by London Dispersion Interactions. Molecules (e.g. pyridine, THF) that are solely bases, that have no ability to donate an acidic proton, lie above the line defined by the non-polars. That excess interaction enthalpy for all 7 bases studied is equal to their heats of hydrogen bonding to p-fluorophenol. The isosteric heat of adsorption of those 7 bases on Illinois No. 6 coal is quantitatively explained by two terms, London forces and hydrogen bonding. There being no need to invoke others, normal scientific practice prohibits it. Contact angle studies also demonstrate that only two terms, dispersion and acid/base interactions, are necessary to describe fully interactions at coal surfaces.¹

Is the situation the same when molecules are dissolved in (absorbed by) solid coals? The interactions of organic molecules when dissolved in coals can be monitored by studying volumetric solvent swelling.⁴ Swelling pyridine-extracted Illinois No. 6 or Pittsburgh No. 8 coals with non-polar solvents gives rise to a symmetrical bell-shaped curve when solvent-swelling ratios are plotted against solvent solubility parameters (see Fig. 1). Plotting the swelling caused by basic molecules using their non-polar solubility parameters generates a set points all lying above the line defined by the non-polars. Furthermore, the excess swelling (the amount by which the swelling by bases is increased above the non-polar line) gives good straight lines when plotted against the bases' heats of hydrogen bonding to p-fluorophenol.⁴ This behavior parallels that observed for adsorption and again only hydrogen bonds and London Dispersion Interactions are required to explain the interaction between dissolved molecules and bituminous coals.

The existence of bell-shaped plots of coal swelling by non-polar solvents and of acetylated coals by all solvents¹ is strong evidence against n - n and charge transfer (CT) interactions. This can be argued in two ways. First, the shape of the plot demonstrates that these systems are following regular solution theory. That theory assumes that there is an averaging of the interactions between the coal and the swelling solvent based on the assumption that only dispersion interactions are occurring.³ Coal-coal, solvent-solvent, and coal-solvent interactions are all assumed to be solely dispersion interactions. Specific complex formation and the interactions that would lead to them are excluded. Second, the solubility parameter of the coal is that value defined by the peak of the bell-shaped curve. The square of that

solubility parameter value is the cohesive energy density of the coal, a direct measure of the coal's self interactions. For all of the bituminous coals studied, these self interactions are of the same order as toluene's or chlorobenzene's, liquids which self interact by London dispersion interactions and electrostatic interactions due to π -dipole or π quadrupole interactions. These bell shaped curves provide evidence against a significant role for π - π stacking and CT interactions in coals.

A qualitative consideration of π - π stacking and CT interactions using perturbation molecular orbital theory⁶ provides a strong argument against their importance in coals. The benzene dimer is a convenient starting point and example. As a pair of benzenes approach each other in a face-to-face orientation, their interaction gives rise to new bonding and antibonding orbitals by overlap of the highest occupied molecular orbitals (HOMO). The energy difference between the HOMO and the lowest occupied molecular orbital (LUMO) is so large that no interaction between them occurs.⁶ The HOMO-HOMO overlap of the two benzene filled orbitals gives rise to new bonding and antibonding orbitals. Both are filled and the fact that the antibonding orbitals increase in energy more than the bonding orbitals decrease results in a repulsive interaction. The interaction of the two benzene π systems is repulsive. The antibonding destabilization is greater than the bonding stabilization. This is a 2-orbital 4-electron repulsive interaction. The benzene dimer is "T" shaped minimizing this repulsion and maximizing quadrupolar interactions.⁷ Theory and experiment agree.⁷

This model can be used to define those circumstances in which pair-wise interactions will be favorable due to electron transfer. First, if the HOMO-LUMO gap is small, then the HOMO and LUMO can interact. This interaction will give rise to a stabilization because only the bonding orbital will be occupied. This 2-orbital 2-electron interaction might be a charge transfer involving a non-bonding pair of electrons or a π - π interaction between an occupied and an unoccupied orbital. It makes no difference: the description is the same. To explore this possibility, the ionization energies and electron affinities of groups present in coals are tabulated in Table 1. The other possibility is a 2-orbital 3-electron interaction that will occur if a radical center is involved. Since the radical demands a half occupied "LUMO" or HOMO (called a SOMO), there is likely to be an orbital of similar energy available. It does not matter whether the interacting orbital is occupied or not. Both will give rise to a stabilization, greater in the case of a 1-electron 2-orbital interaction than in the case of a 3-electron 2-orbital interaction. The radical centers in coals may be the loci of strong interactions. This possibility is under investigation.

A consideration of the electron affinities (EA) and ionization potentials (IP) in Table 1 leads to the conclusion that π - π and CT interactions in coals are unlikely to be favorable. The HOMO-LUMO gaps are too large to allow CT to occur. This is supported by experiment. Consider first the interactions between several organics and tetracyanoquinodimethane (TCNQ), an electron acceptor with an EA about 50 kcal/mole more favorable than pyrene. The equilibrium constant for complex formation between pyrene and TCNQ is only 29 l/mole.⁸ With materials of lower electron affinity, the equilibrium constant will be even less. For the materials contained in the table, the HOMO-LUMO gap is so large that π - π and CT interactions are unimportant. The HOMO-LUMO gap remains large enough for all reasonably sized molecules to rule out stabilization by electron transfer interactions.

There are numerous experimental and theoretical studies of aromatic-aromatic interactions.⁹ To begin with theory, molecules as large as circumcoronene ($C_{54}H_{18}$) have been studied.¹⁰ Even here, the HOMO-LUMO gap is large enough so that the dominant attractive interactions are dispersion and electrostatic. The most favorable calculated geometry is not face-to-face but displaced and twisted. Effective theory has been developed and applied to numerous aromatic systems.^{7,9,11} It uses attractive dispersion and electrostatic (dipolar and quadrupolar) interactions and repulsions originating from π - π interactions.

There are numerous experimental studies of aromatic-aromatic dimers and multimers, most formed using molecular beam techniques.⁹ The geometries vary depending on the nature of the interactions and especially on any charge separation in the molecules. The range from "T" shaped, to a " π " shaped trimer¹², to face-to-face coplanar dimers^{13,14} where dipolar and quadrupolar interactions are most favorable in this geometry.¹⁵ In none of these is the primary interaction due to ground state electron transfer.

The principal attractive interactions between pairs of aromatic systems depends on the polarizabilities and dipole and quadrupole moments of the interacting systems. The filled orbital interactions are repulsive. This issue and others will be discussed in a full paper together with the evidence (or lack thereof) for π - π stacking and CT interactions in coals.

Figure 1. Volumetric swelling ratio (Q_v) for pyridine extracted Bruceton coal as a function of the solubility parameter of the non-polar solvents (\bullet) and the non-polar stability parameter of the polar solvents (\circ)

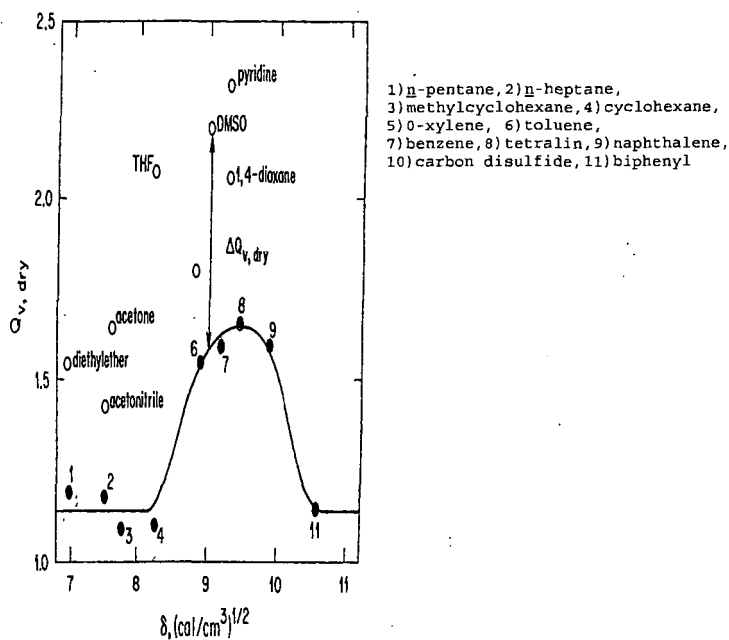


Table 1. Molecule Ionization Potentials (IP) and Electron Affinities (EA)

Molecule	IP (eV)	EA (eV)
Benzene	9.24 ^a	-0.72 ^b
Naphthalene	8.15 ^a	0.15 ^b
Anthracene	7.42 ^a	0.66 ^b
Phenanthrene	7.90 ^a	0.31 ^b
Pyrene	7.43 ^a	0.56 ^b
Pentacene	6.66 ^a	1.35 ^b
Coronene	7.36 ^a	
Phenol	8.51 ^c	-1.01 ^d
Aniline	7.7 ^c	-1.13 ^d
Pyridine	9.3 ^c	-0.62 ^d
Maleic Anhydride		1.33 ^e
TCNQ		2.84 ^e
TCNE		2.77 ^e
CS ₂		0.90

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NOVEL DIMENSIONS IN ON-LINE PROCESS SPECTROMETRY

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INTRODUCTION

The myriads of novel chemical processes the new millennium may be expected to bring to future generations will require increasingly sophisticated process characterization and monitoring techniques. Over the past decades the advantages of on-line, in-situ and/or real-time spectrometric techniques have been widely demonstrated. The main challenges for the new millennium will be: to achieve higher information yields and sample throughputs; to develop intelligent devices that interpret their own measurement data; to close the feedback process control loop; to probe harsh reaction environments in real-time; and to reduce total lifecycle costs for on-line spectrometry equipment.

INCREASING INFORMATION YIELD AND RATE

As discussed convincingly by Hirschfeld [1] and by Giddings [2], the most effective way to achieve higher information yields is to couple two or more compatible analytical techniques into a single "hyphenated" tandem method. Well documented examples include GC/MS, LC/MS, MS/MS, GC/IMS and GC/FTIR. (It may be noted that the term "hyphenated" - popularized by Hirschfeld - is somewhat of a misnomer since IUPAC nomenclature prescribes the use of forward slashes rather than hyphens to depict tandem instrument configurations). Hyper-hyphenated methods, featuring as many as four different analytical instruments in tandem have also been described, e.g. TG/GC/FTIR/MS [3]. Even more analytical dimensions can be added through "tandem-in-time" configurations such as in ion trapping MSⁿ methods, with *n* readily achieving values of 6 or 7 [4]. Also, it should be pointed out that as many as four useful analytical dimensions can be added by recording temporally [5] as well as spatially resolved spectra. An example of the use of time-resolved, on-line MS data to deconvolute a complex mixture of coal pyrolysis products, evolving from a small Curie-point pyrolysis reactor, into its main maceral constituent patterns, is shown in figure 1.

Unfortunately, our ability to add analytical dimensions has greatly outpaced our ability to process and interpret multidimensional data. Some progress is being reported in the development and application of principal component analysis techniques for three-way data matrices [6]. Also, the class of algorithms loosely described by the term ANN (artificial neural networks) is in principle capable of handling *n*-dimensional data outputs [7]. However, most of us are still struggling to comprehend multivariate data analysis results for two-way data matrices. Clearly, processing and interpretation of *n*-way data matrices is an area with much room for progress in the new millennium.

Whereas hyphenated methods are widely known for their ability to increase information yields, less well recognized is their potential for increasing analysis speed. At first sight it is counterintuitive that the coupling of two instruments in tandem could produce shorter analysis times. However, as pointed out by Giddings [2], to the extent that the information provided by independent, the resolving power of the tandem instrument equals the product of the resolving powers of the two modules. Since many analytical techniques can trade resolving power for speed the required minimum resolution for a given analytical application can often be reached with both modules operating in a high speed, low resolution mode, as illustrated in figure 2.

Interestingly, low resolution analytical modules also tend to be easier to miniaturize (or, perhaps more correctly stated, miniaturization tends to result in lower resolution) leading to the paradoxical conclusion that hyphenated methods may well lend themselves better to miniaturization and micro-miniaturization and, thus, to use as on-line analytical devices. The added complexity of the control electronics and software required to control hyphenated devices versus single stage modules may hardly increase the size and cost of large-scale-integrated electronic chips. In short, the future for hyphenated techniques in on-line process analytical applications is likely to be equally bright as in today's conventional analytical laboratory environment where the majority of new GC systems purchased is now equipped with an MS "detector".

PROBING HARSH REACTION ENVIRONMENTS

The suitability of stand-off spectroscopic techniques for probing high-temperature, high-pressure, high-radiation, highly corrosive and/or abrasive environments is widely known and is only limited

by the relatively low resolving power for complex chemical mixtures, by the availability of suitable window materials, and by the optical properties of the reactor contents. Since continuing progress can be anticipated in all these problem areas, the role and importance of stand-off spectroscopic process analysis techniques may be expected to help increasing over the next few decades.

Compared to stand-off techniques, the suitability of typical point detection methods (i.e. methods requiring physical transport of molecules, sampled at a given point in space and time, into the detector) for probing harsh reaction environments is less immediately obvious. Yet, the superior separation and identification capabilities of point detection methods such as MS (with or without chromatographic pre-separation) have time-and-again induced scientists and engineers to use MS-based methods in highly forbidding environments. An example of the use of on-line GC/MS for monitoring a 600 F flue gas stream, laden with abrasive ash particles, on the 7th floor of a rumbling, dusty coal combustor situated in a building subject to circadian temperature variations in excess of 50 F, is shown in figure 3.

Fortuitously, the use of rugged sample probes lined with fused silica, quartz or other refractory materials is often compatible with the required operating conditions for a given point detector, particularly in combination with highly flexible, readily heatable, capillary transfer lines. This approach enables successful coupling of GC/MS instruments to reactor environments with pressures in the several thousand psi range, including supercritical environments (see figure 4) and temperatures in excess of 1800 F [8]. Nonetheless, there is considerable room for further improvement in sample transport systems, e.g. capable of entraining fine particulate matter indigenous to the sample stream or produced with the help of ablative laser probes. Another, as yet unexplored, sampling strategy would be to enlist the support of "stand-off sampling techniques" for point detectors, e.g. by shooting fast traveling vortices, capable of entraining vapors as well as fine particulate matter, across reactors into the point detector inlet.

REDUCING INSTRUMENT LIFECYCLE COST

Most on-line spectroscopic techniques have a reputation for high capital equipment cost, very high maintenance cost and exorbitantly high operating cost (due to the need for highly trained operators). As a result most production managers are understandably reluctant to introduce novel spectroscopic techniques into existing process operations unless there are serious problems. Consequently, new opportunities for on-line spectroscopic techniques must primarily may need to be sought in the development and testing of novel processes and pilot plants.

Recent breakthroughs in the design of highly miniaturized and/or microfabricated MS analyzers promise to drastically change the instrument lifecycle cost equation for this type of analyzer within the next few years. Not only are these miniaturized MS analyzer modules (including ion source and detector) likely to become available commercially at a cost of less than US \$1,000 but — due to the difficulty of exchanging or cleaning the very small ion source or detector components — they are also meant to be disposable in case of failure or deterioration. The big advantage of this approach is its potential to greatly reduce overall maintenance cost.

Presently, no fewer than three such disposable MS devices are either already available (viz. Ferran's miniature quadrupole head [9]), or may become available soon (viz. a subminiature double focusing magnetic device and an FTICR type MS device; both expected to be introduced at the January 2000 ASMS conference in Sanibel). Present limitations include limited resolving power (i.e. the product of mass range and resolution), as well as relatively low sensitivity and/or speed. As discussed earlier, hyphenation (e.g. by adding a micro-GC preparation module) may eventually help overcome some of these limitations. A related area where major improvements will be needed to match these new developments in MS analyzer technologies is high vacuum pumping. Current high vacuum pump technology is expensive and difficult to miniaturize further.

Finally, the major cost of using on-line spectroscopic techniques, viz. the need for highly trained operators, is only going to come down when the above-mentioned multidimensional data processing and interpretation steps can be fully automated and integrated into the design of the spectroscopic instrument. In other words, development of sufficiently "smart" spectroscopic devices is likely to be the final hurdle on the way to broad acceptance of on-line spectroscopic technologies into the full scale process analysis marketplace.

CONCLUSION

Rapid development of MS-based and other miniaturized and micro-miniaturized, MS based on-line spectroscopic methods can be expected over the next few decades, eventually resulting in the presence of multiple, networked, disposable, hyphenated devices per reactor. The temporally and

spatially resolved information produced and processed by the network will allow an unprecedented degree of process control and quality assurance, as well as rapid troubleshooting capability if and when human intervention becomes necessary.

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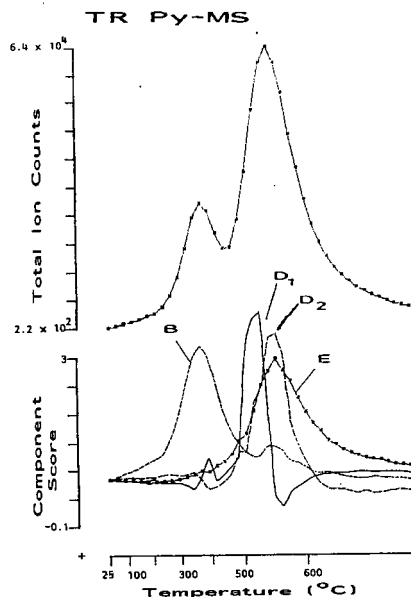


Figure 1. Example of the use of time-resolved mass spectral profiles to produce an additional analytical dimension. The total ion profile in (a), representing Curie-point pyrolysis products evolving from a coal sample, is being deconvoluted into four maceral-like components (b) by means of multivariate statistical analysis methods. For detailed information see reference 5.

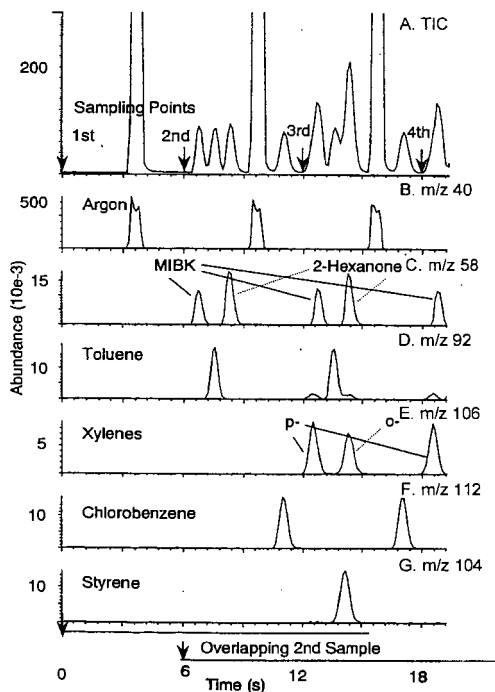


Figure 2. Example of fast, repetitive hyphenated (GC/MS) analysis demonstrating complete resolution of 9 components in 2-dimensional (GC/MS) space although the individual component techniques resolve only 5 (GC) and 7 components (MS), respectively. For detailed information see reference 10.

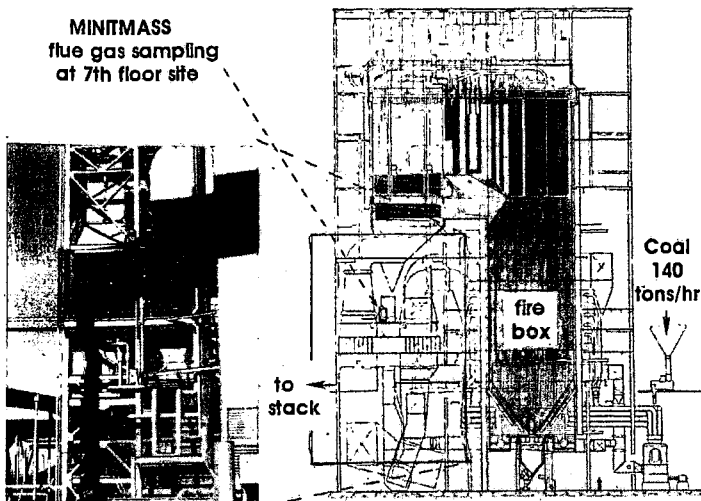


Figure 3. Example of operating a GC/MS instrument, nicknamed "minitmass," in a harsh industrial environment.

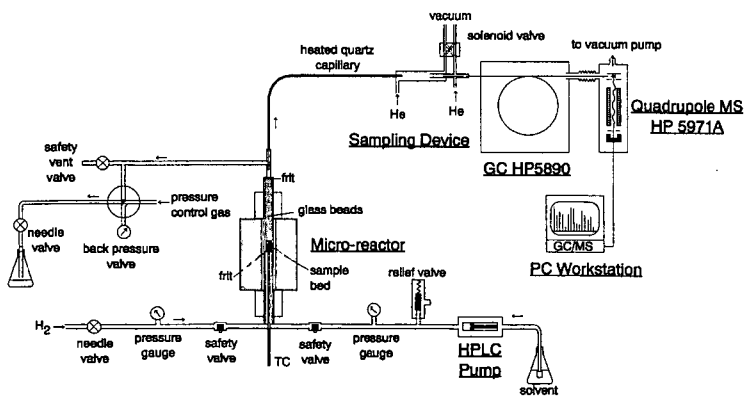


Figure 4. Example of an on-line GC/MS experiment coupled to a bench-scale high pressure reactor operating under supercritical conditions. For detailed information, see reference 8.

THE CHAMELEONIC CARBON SURFACES: ENVIRONMENTAL PROBLEMS AND SOLUTIONS

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1. INTRODUCTION

Among the fossil fuels, the negative environmental impact of coal is typically larger than the impact of either petroleum or natural gas. Considerations of both conventional pollution (acid rain and smog) and global warming (presumably caused by CO₂ accumulation in the atmosphere) cast serious doubts on the continued massive use of coal in the 21st century. A simple back-of-the-envelope calculation illustrates the complexity of the problem. While bringing an economic boom to states such as Wyoming, the ongoing market switch from higher-rank, high-sulfur coals (ca. 200-250 lb CO₂/10⁶ BTU) to lower-rank, low-sulfur coals (ca. 300-350 lb CO₂/10⁶ BTU) is making the global warming problem even worse:

$$\frac{72\text{lbC}}{100\text{lbCoal}} \frac{44\text{lbCO}_2}{12\text{lbC}} \frac{1\text{lbCoal}}{8000\text{BTU}} = 330 \frac{\text{lbCO}_2}{10^6 \text{BTU}}$$

$$\frac{82\text{lbC}}{100\text{lbCoal}} \frac{44\text{lbCO}_2}{12\text{lbC}} \frac{1\text{lbCoal}}{14000\text{BTU}} = 215 \frac{\text{lbCO}_2}{10^6 \text{BTU}}$$

While the politics of this issue are daunting -- it remains to be seen how the world will prevent China and India from using coal to fuel their expected economic boom in the 21st century and whether the U.S. will find cost-effective alternatives to coal for electricity generation -- here we shall explore a new concept in carbochemistry (vs. petrochemistry), as an alternative "high-tech" way of continuing to use the world's vast coal resources. We are not advocating the return to carbochemistry of the 19th century, when coal was the source of organic chemicals which gave birth to chemical industry (1). Our main focus is on the fact that the 20th century has ushered in the "age of materials" (2, 3). We argue that a realistic path toward the appealing "natural capitalism" advocated by Amory Lovins for the 21st century (4) naturally includes an increasing role for coal-derived carbons. We are thus proposing a novel concept in coal conversion (see Figure 1): the production of high-value-added carbon materials from *all* of its fractions. The key distinguishing feature of this concept is not that coal will be the raw material for the production of low-cost, high-performance materials such as carbon fibers, even though "Natural Capitalism" advertises these products as a panacea (4). Rather, the novelty of the concept is illustrated in Figure 2. Previous coal conversion concepts were based on tailoring the process toward the manufacture of one or two products; the residue, often a very large fraction of the coal, was then used as a fuel or was discarded. For example, in "mild gasification" (actually coal pyrolysis), which was a popular concept a decade ago, coal-derived liquid fuels are the desired product but the residual char, used as fuel, can represent as much as 70% of the product. There will be no residue in the processes whose concept is being advocated here. As illustrated in Figures 1 and 2 and discussed in more detail below, the processing steps and the intermediate products will be optimized in such a way that each end-product will find a market where its properties will be in most cases superior or at least comparable to existing products. The principal markets (see Figure 1), which are expected to be big in the 21st century and are natural outlets for coal-based products, are specialty adsorbents, catalysts, electrodes and electrocatalysts. While the required properties for these materials differ in many important details, they have one important commonality: in addition to optimized physical surface properties (i.e., a specific pore size distribution), superior performance requires careful tailoring of their chemical surface properties (5).

2. COAL-TO-CARBON CONVERSION

This is envisioned as a fractionation process akin to that of coal liquefaction. Taking advantage of the vast industry experience, the products are grouped into preasphaltenes, asphaltenes, oils and (heptane-) insolubles. The conditions we advocate are typical to those often encountered in coal liquefaction, but there is no insistence on maximizing the yield of oils, and thus the expected costs (see Section 7) are not as vulnerable as those of coal liquefaction: <1000 psi N_2 or H_2 , 620-670 K, using a process-derived solvent. The post-fractionation processing steps are discussed below. The feedback loop in Figure 1 illustrates the key issue: do the process conditions used and the selection of a particular coal result in an optimum yield and quality of the intermediate and final products? The affirmative answer to this question relies on our ability to practice molecular engineering by heat treatment of the fractions and chemical modification of the intermediate products (see Figure 1). This in turn gives us the ability to control crystallite alignment and property anisotropy development in the final products. The optimum yield issue is briefly addressed in Section 7. The quality issue is outlined in Sections 3-6.

3. SPECIALTY ADSORBENTS FROM COAL

Coal-derived activated carbons for air and water cleanup have become commodity products, at a typical cost of \$1/lb. There is now some irony in future developments: the research required for better products is hampered by this commodity status and by global-economy competition. And yet the increasingly stringent legislation on clean air and clean water do require vast improvements in the performance of activated carbons. The way out of the impasse is the development of specialty adsorbents. In recent years it has become obvious that in the use of carbons for water treatment in particular (e.g., removal of phenols), but also for removal of gases and vapors where at least interfering moisture effects are present (e.g., SO_x and NO_x removal from air, gas storage), the chemistry of the adsorbent surface is often the dominant factor (6, 7). Both the nature of the coal and the conditions of coal and carbon processing are highly adaptable to the production of a desired surface chemistry in the final product. Thus, for example, all the intermediate products except oils (see Figure 2) are suitable precursors for specialty carbon adsorbents. Their porosity and surface area development ("activation") may not require a preoxidation step (as is the case in conventional preparation of activated carbons from bituminous coals) and their chemical modification can make the surface either highly acidic (and hydrophilic) or highly basic (and hydrophobic).

4. CATALYSTS FROM COAL

Carbon materials are known to have unique properties in catalysis, both as supports and as catalysts in their own right (8, 9). Even though this is a relatively mature market, almost as mature as that of activated carbons, the opportunities for tailoring chemical surface properties for optimum performance are practically virgin territory. The issues here are similar to those outlined in Section 3: catalytic activity depends at least on the surface area of the catalyst, which in turn can be tailored by optimizing the surface chemistry and physics of the support. But it also depends on the electronic structure of the carbon, either directly (electron transfer in the catalyzed reaction of interest) or as a consequence of the often desirable catalyst/support interaction. Two examples will suffice to illustrate the tremendous opportunities here for coal-derived carbons. In the pharmaceutical and fine-chemicals industries, carbon-supported noble metal catalysts are widely used and yet poorly understood; in the processing scheme shown in Figure 2, each one of the products will have a unique combination of bulk (e.g., electronic) and surface properties, depending on the degree of carbon crystallite growth and alignment, which is controlled in turn by selecting the starting coal and the processing conditions. Even carbons produced by vapor cracking (e.g., P3 in Figure 2), used without surface modification, offer unique catalytic properties; a good example is the family of oxidative dehydrogenation reactions (e.g., of ethylbenzene), where carbon is now known to play a key role (8, 10) even though the (nominal) catalyst is alumina-based.

5. ELECTRODES FROM COAL

The necessary combination of optimized bulk and surface properties, which is generated naturally in the coal-derived carbons proposed here, is a *sine qua non* condition in high-performance electrodes. Here we have in mind not so much the conventional markets (e.g., steel and aluminum manufacturing); we see untapped opportunities primarily in the booming and yet very deficient market of rechargeable batteries (11) and supercapacitors. Because this is such an interdisciplinary application, with required inputs from coal and materials scientists, as well as from carbon scientists and electrochemists, successful development of (ash-free) superior products will be possible only through implementation of the *entire* spectrum of carbon characterization tools shown in Figure 1.

6. ELECTROCATALYSTS FROM COAL

This is the holy grail of energy science and technology. It is also the ultimate challenge for carbon science and technology and it is here that the proposed concept can provide the much needed breakthroughs. Carbon materials are currently used (12, 13) and misused (14) in several types and components of fuel cells. In the "hot" field of polymer-electrolyte-membrane fuel cells, for example, they are not only the electrodes and current collectors but also the diffusion layers and electrocatalyst supports. In each application, the right combination of porous structure, surface chemistry and proton and electron transfer characteristics is required. There is no better opportunity than that afforded by the concept proposed in Figures 1 and 2 to achieve this goal: a cost-effective, high-performance, even perhaps a non-noble-metal carbon-supported electrocatalyst for the reduction of O₂ (as well as hydrogen and/or hydrocarbons).

7. SUMMARY: TECHNO-ECONOMIC OPTIMIZATION

The oversimplified but illustrative equation presented below highlights the key advantage of the proposed concept (see Figure 2).

$$Max \frac{\$}{yr} = \frac{OptlbP1}{yr} \frac{\$}{lbP1} + \frac{OptlbP2}{yr} \frac{\$}{lbP2} + \frac{OptlbP3}{yr} \frac{\$}{lbP3} + \frac{OptlbP4}{yr} \frac{\$}{lbP4}$$

The aromatic character of coal makes it a natural, high-yield raw material for carbon products. And the chameleonic nature of the carbon surface, which can be tailored to produce a variety of either bulk-property-dominated materials (e.g., P3) or surface-active materials (e.g., P1, P2, P4), provides the desired flexibility in exploiting the emerging markets of the 21st century. Both the yields of the products (OptlbP/yr) and their quality or market value (\$/lbP) can thus be optimized and continually fine-tuned for maximum profit (Max\$/yr). This augurs well for an elegant scientific, technological and economic solution to the environmental problems of coal utilization.

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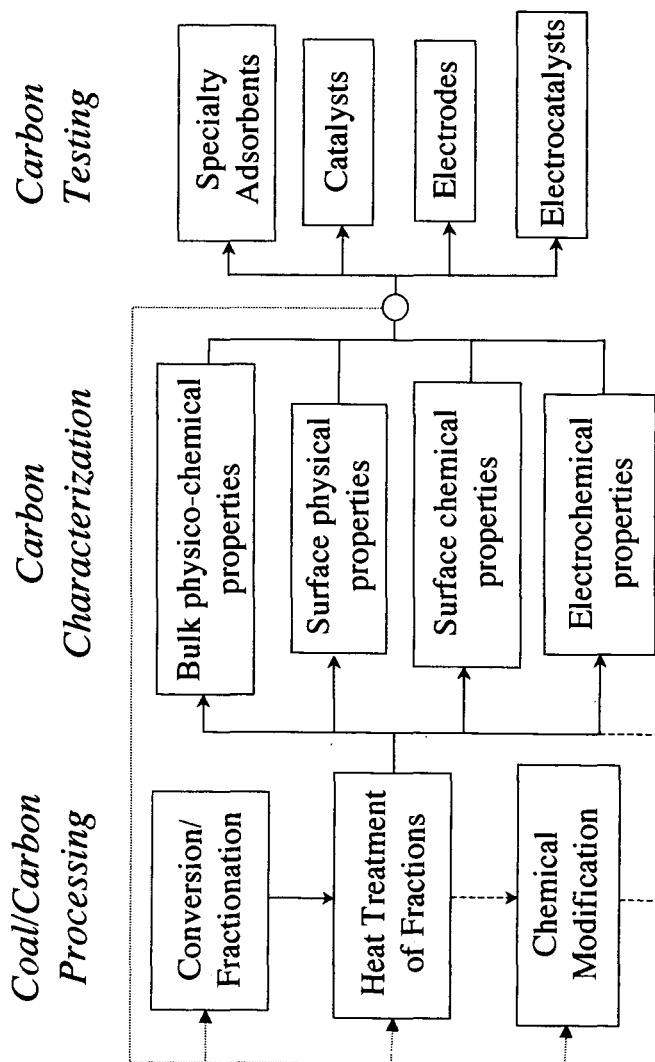


Figure 1
R&D flow diagram of an environmentally benign, technologically novel and economically flexible process of coal utilization by complete conversion to high-value-added carbon materials.

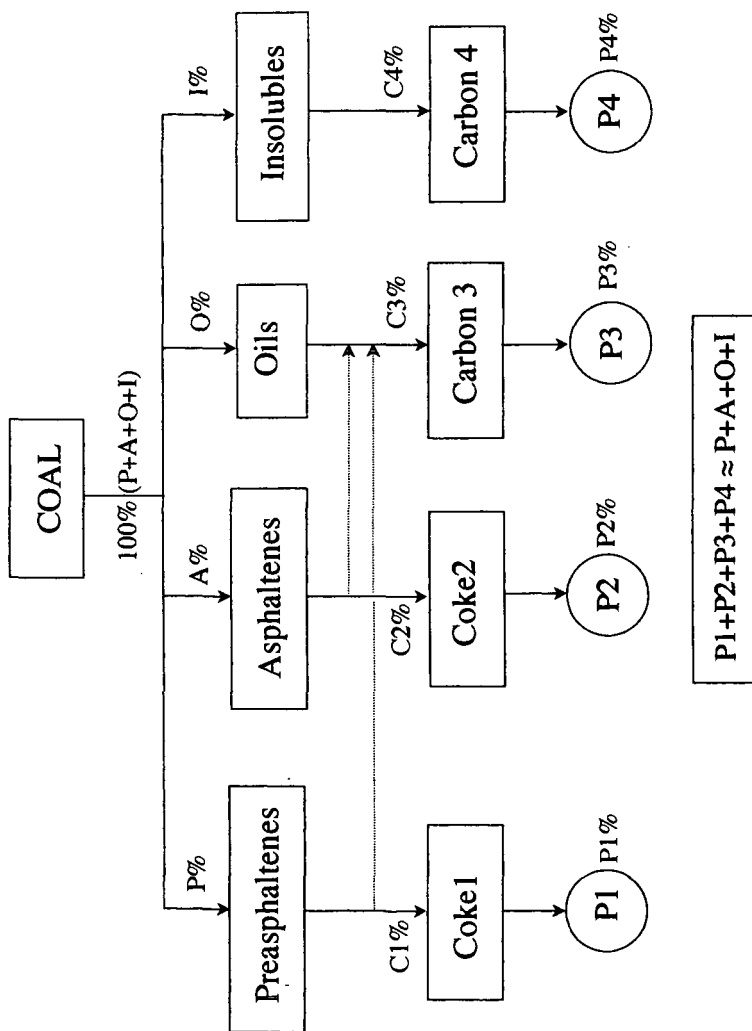


Figure 2. Optimization of the yields of end-products (P1-P4) in the complete conversion of coal to high-value-added carbon materials.